Effect of HCl on Starch Structure and Properties of Starch-based Wood Adhesives

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Starch-based adhesive was prepared from corn starch and polyvinyl alcohol (PVA) as raw materials by acid hydrolysis with HCl. The starch was hydrolyzed with different amounts of HCl and characterized using Fourier transform infrared spectroscopy, X-ray diffraction, scanning electron microscopy, and thermal gravimetric analysis. The results indicated that different amounts of HCl affected hydrogen bonds, the amount of free hydroxyl groups, crystalline structure, compatibility between starch and PVA, thermal stability, and bond strength. The crystallinity decreased by 13.7% when the amount of acid was 33% compared with untreated starch. The bond strength reached its maximum of 1.35 MPa when the acid content was 23%. The initial decomposition temperature of starch decreased after acid hydrolysis. It was also noted that corrosion of the starch surface increased with increasing acid content.

Keywords: Starch-based adhesive; Structure and properties; Amount of HCl

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INTRODUCTION

Starch is one of the most abundant natural, renewable, and biodegradable polymers and is produced by plants as a source of energy. In recent years, starch has attracted much attention as a raw material for producing wood adhesive because of its low price, abundance, non-toxicity, and renewable, biodegradable properties. It is necessary to modify starch to change its viscosity and solubility, as well as to improve other relevant properties when it is used for preparing starch-based adhesive. Liu *et al.* (2004) reported that the water resistance of starch-based adhesive was improved by oxidizing, condensing, and crosslinking the starch component. Wu *et al.* (2008) developed a starch-based adhesive by grafting monomers, such as vinyl acetate and butyl acrylate, onto the main chains of starch with ammonium persulfate as an initiator. Acid-hydrolysis is an effective method for treating starch for preparing starch-based adhesive (Hoover 2000). Shi *et al.* (2009) prepared a starch emulsion by hydrolyzing starch with HCl and oxidizing it with ammonium persulfate. Sun *et al.* (2004a) hydrolyzed corn starch and potato starch with HCl. The acid-hydrolyzed products were characterized using iodimetry, X-ray diffraction, and differential thermal analysis. Zuo *et al.* (2012) investigated the crystallinity and thermal properties of starch after acid hydrolysis, and the viscosity and temperature when starch is gelatinized. Thys *et al.* (2008) reported on the effect of acid concentration on the structure of hydrolyzed starch.

The objective of this study was to develop a series of starch-based adhesives by hydrolyzing starch with HCl. The study focused on the effect of HCl content during hydrolysis on the properties of the produced adhesive. Fourier transform infrared (FTIR) spectroscopy, X-ray diffraction (XRD), scanning electron microscopy (SEM), and thermogravimetric analysis (TGA) were used to analyze the chemical and physical structures of treated starch. The bond performance of these adhesives was also evaluated.

EXPERIMENTAL

Materials

Corn starch was supplied by Shandong Hengren Industry Corp. (Shandong, China). PVA (PM 1799/1788) was provided by Tianjin Yongda Chemical Reagent Corp. (Tianjin, China). HCl and sodium hydroxide (NaOH) were purchased from Jiangsu Dongsheng Chemical Reagent Corp. (Jiangsu, China). pMDI was obtained from Bayer Co. (Tianjin, China). All other reagents were of analytical grade.

Methods

Preparation of starch-based wood adhesive

Adhesive preparation was carried out in a three-necked, round-bottom flask equipped with a condenser, a stirrer, and a thermometer. PVA-1788, PVA-1799, starch, and deionized water were added to the flask. The mixture was hydrolyzed with various amounts of HCl at a certain temperature and for a certain duration. The amounts of HCl added to the hydrolysis system were 13%, 18%, 23%, 28%, and 33%, based on the amount of starch added to the system. The hydrolyzed starch was treated with 30% sodium hydroxide solution for a given period of time. The crosslinking agent (pMDI) was added to the treated starch at a 5/1 (w/w, starch/pMDI) ratio before the starch-based wood adhesives were used.

Fourier transform infrared spectroscopy (FTIR) measurement

The original corn starch and treated starch samples were dried and milled with KBr before being pressed into a thin sheet for FTIR analysis using an IRPrestige-21 FTIR spectrometer (Shimadzu Corp., Japan). Each sample was scanned 32 times from 4000 to 500 cm^{-1} at a resolution of 4 cm^{-1}.

X-ray diffraction (XRD) measurement

The X-ray diffraction data were collected at room temperature using an XRD-6000 diffractometer (Shimadzu Corp., Japan) with CuKα radiation operating at 40 kV and 30 Ma. The corn starch and treated starch samples were tested. The treated starch was freeze-dried and cut into small pieces. The test samples were made by pressing the pieces into slices. All samples were scanned from 5 to 40° at a scanning speed of 5°/min with a step size of 0.04°. The relative crystallinity of the samples was calculated using the machine's software.

Scanning electron microscopy (SEM) measurement

Images showing the granular morphology were obtained using a TM-1000 SEM (Hatachi, Ltd., Japan) operating at 15000 kV accelerating voltage. The freeze-dried treated starch and untreated starch samples were mounted on an aluminium specimen holder with double-sided carbon tape and sputter-coated with a thin gold film.

Thermogravimetric analysis (TGA)

Thermogravimetric analysis was conducted using a STA409c thermal analyzer (NETZSCH, Germany). The samples were freeze-dried, and about 5 to 10 mg were weighed for measurement. The heating rate was 10 °C/min, and the measured temperature range was from 25 to 600 °C.

Lap shear strength test

The lap shear (bond) strength of the adhesive was tested according to Chinese industry standard GB/T 17657-2006. Wood veneers with 1 mm thickness were cut into rectangles with dimensions of 2.5×10 cm^2. Adhesive was applied to one side of each piece of veneer. The adhesive-coated area was 2.5×1.3 cm^2 at one end of each veneer. The spread rate of the adhesive was 240 g/m^2. The coated areas of two adhesive-coated veneers were overlapped with their grains parallel to each other and pressed with 0.45 MPa pressure and 25 °C for 72 h. The bonded samples were soaked in hot water (63 °C) for 3 h before shear testing. The shear test was carried out using a MWD-100 universal mechanics testing machine (Jinan Times Shijing Corp., China) while the samples were still wet. The test speed was 1 mm/min. Twelve replicates were tested for each condition.

RESULTS AND DISCUSSION

Structural Analysis of Treated Starch

Fourier transform infrared spectroscopy analysis

The FTIR spectra of untreated and treated starch are shown in Fig. 1. The spectra show that hydroxyl group absorption in the starch occurred at approximately 3481 cm^{-1}, but the hydroxyl absorption in the treated starch samples occurred between 3500 cm^{-1} and 3400 cm^{-1}, and the peaks became narrower. This suggests that the treatment with acid broke the hydrogen bonds between the starch molecules and increased the number of free hydroxyl groups, leading to the peaks shifting to the left and becoming sharper.

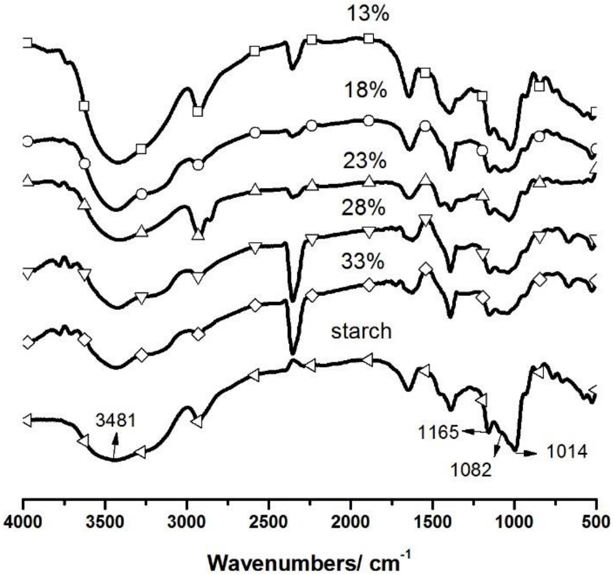


Fig. 1. FTIR spectra of untreated and treated starch with different amounts of HCl

The intensity of the hydroxyl peak first increased, then decreased after reaching a maximum when the amount of HCl was increased, which was in agreement with the results of bond strength testing. The bands at 1082 cm^{-1} and 1165 cm^{-1} were the bending vibration absorptions of the C-O-C and C-O bonds of the glycosidic linkages in the starch. The band at 1014 cm^{-1} was the deformation vibration absorption of C-O-H and C-O bonds (Goodfellow and Wilson 1990). The intensities of these peaks visibly decreased in the treated starch samples because the treatment with acid resulted in the breakage of glycosidic bonds.

X-ray diffraction analysis

The X-ray diffraction patterns of treated and untreated starch samples (Fig. 2) show peaks at 2θ values of 15.06°, 17.10°, 18.06°, and 23.02°, and its crystallinity pattern was A-type (Goodfellow and Wilson 1990). After treatment, the absorption peaks did not change shape but became generally dispersed. The peak at 2θ = 17.10° became weaker, while the peak at 2θ = 18.06° became stronger because acid hydrolysis occurred first in the amorphous part of the starch molecule, forming short molecular chains from the broken molecular chains. These short chains easily rearranged to form small lattices of microcrystals, resulting in a stronger peak at 2θ = 18.06°.

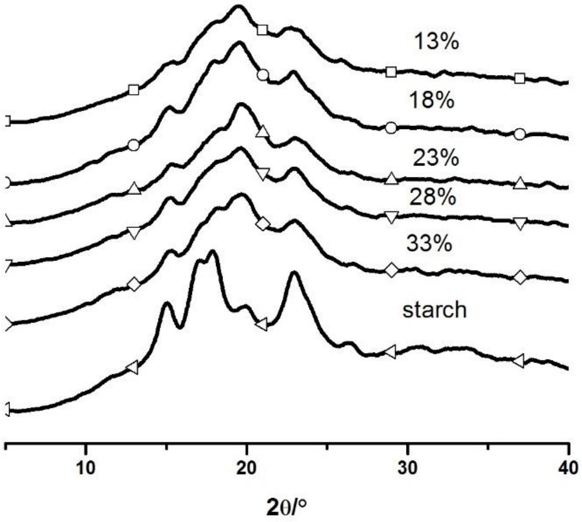


Fig. 2. XRD patterns of treated and untreated starch with different amounts of HCl

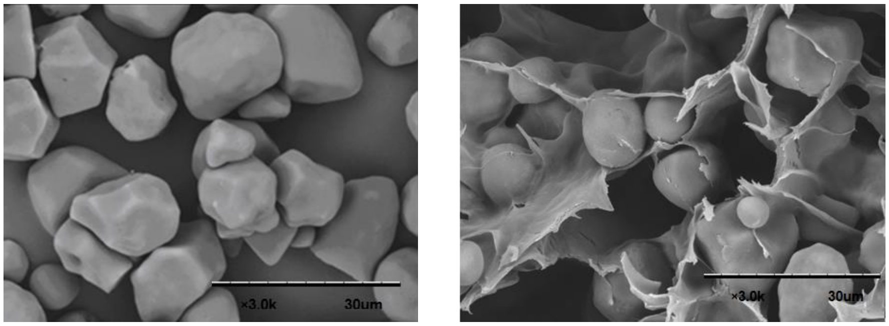
Table 1. Crystallinity (%) of Treated and Untreated Starch

		Crystallinity (%)
	Untreated Starch	57.0
Treated starch with different acid contents (%)	13%	53.3
	18%	54.1
	23%	53.9
	28%	52.4
	33%	50.1

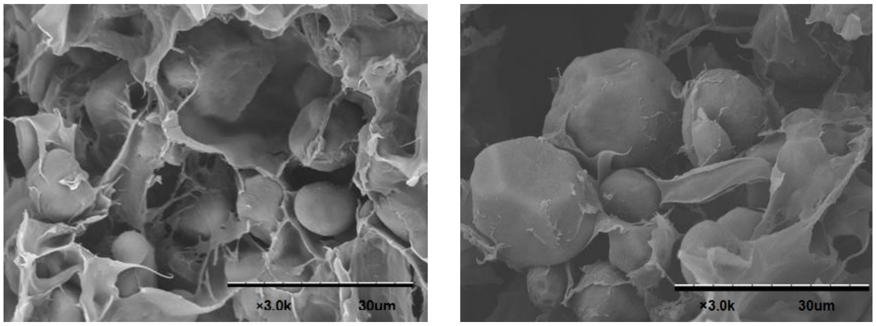
The crystallinity of treated and untreated starch samples with various amounts of HCl were calculated from the X-ray diffraction data, as listed in Table 1. The crystallinity of treated starch first increased, reached its maximum value when the amount of HCl was 18%, and then decreased when the amount of HCl was further increased. Generally, the crystallinity of the treated starch samples was lower than the untreated starch. Acid hydrolysis is generally faster in amorphous regions than in crystalline regions. However, the hydrolysis in crystalline regions increased more when the amount of HCl was further increased, resulting in a decrease in crystallinity.

Scanning electron microscopy analysis

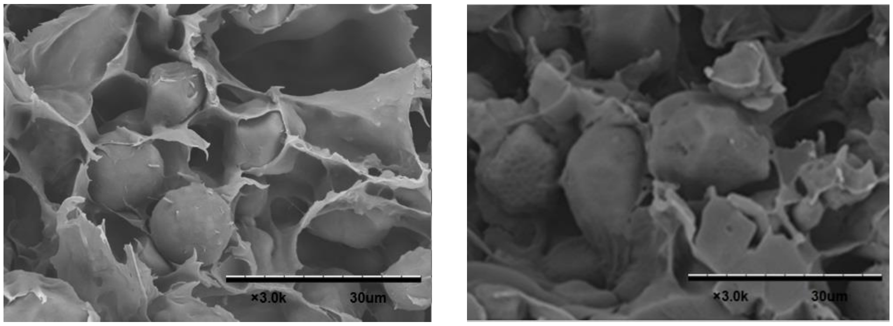
Figure 3 shows SEM photos of the untreated starch and acid-treated starch samples (enlargement rate=3K). The untreated corn starch contained dispersed or agglomerated particles that were irregular polyhedrons with smooth surfaces.



Corn starch (untreated) Starch (HCl=13%)



Starch (HCl=18%) Starch (HCl=23%)



Starch (HCl=28%) Starch (HCl=33%)

Fig. 3. SEM images of treated and untreated starch

The surfaces were corroded when starch was treated with acid. The degree of corrosion was similar with various amounts of HCl, but was lower at 13% of HCl. The surfaces became rough after acid-hydrolysis because the crystalline regions were located on the surfaces of the starch particles, while the amorphous regions were located inside of the particles. Both regions were acid-hydrolyzed to various extents, resulting in rough surfaces (Sun *et al.* 2004a). The starch particles were covered with PVA. The coverage generally increased first, and then decreased when the amount of HCl was increased. The coverage depended on the grafting degree between the starch and PVA, and the grafting degree increased first, then decreased with increasing amounts of HCl. It was found that the coverage was highest when the HCl content was 18%.

Thermogravimetric analysis

The results of thermogravimetric analysis (TGA) are shown in Fig. 4. Differences in curves between the treated and untreated starch were evident, indicating that acid-hydrolysis affected the structure and heat resistance of starch. There were two weight loss sections for all curves. The first weight loss at temperatures close to 100 °C was small and was attributed to water evaporation and the volatilization of small molecules from the samples. The second weight loss, between 260 and 480 °C, was significant and was caused by the degradation of the starch macromolecules (Wang *et al.* 2012).

The shapes of curves among the treated starch samples were similar, but the initial degradation temperatures were slightly different, and lower than those of untreated starch. This suggests that different amounts of HCl affected the heat resistance of starch, but the effect was not significant.

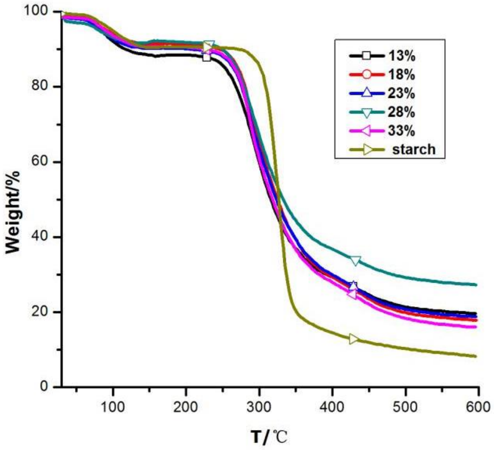


Fig. 4. TGA curves of treated and untreated starch samples

Effect of Amount of HCl on Bond (Shear) Strength

Figure 5 shows the bond strength of modified starch-based adhesive with and without pMDI with various amounts of HCl. The bond strength of adhesive without pMDI was very low, while the bond strength increased significantly when pMDI was added into the adhesive systems. This suggests that pMDI played a key role in improving the bond strength, particularly the wet bond strength, because pMDI reacted with the hydroxyl groups in starch to the formation of a crosslinked network that can keep the bond strength under wet conditions (Shi *et al.* 2008). The network of hydrogen bonds in starch-based adhesive without pMDI cannot withstand the attack of water, resulting in very low bond strength under wet conditions.

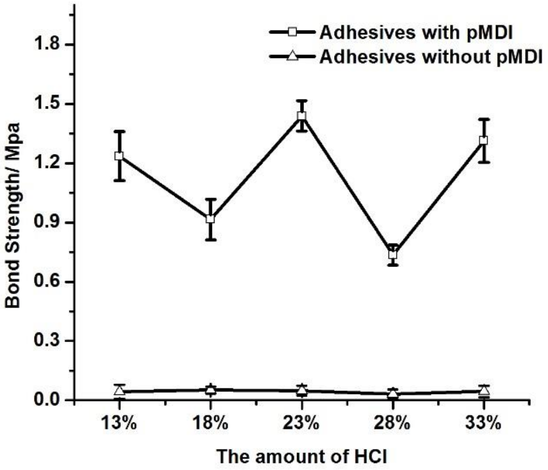


Fig. 5. Shear strength of starch-based adhesive with various amounts of HCl

The bond strength of adhesive with pMDI varied with different amounts of HCl because the bond strength was affected by the amount of free hydroxyl groups in starch molecules. Shi *et al.* (2008) suggested that the unreacted hydroxyl groups in the adhesive increased interactions between the adhesive and wood molecules and improved the bond strength. Acid treatment destroyed the microcrystals in the starch, hydrolyzed the glycoside bond, reduced the molecular weight of starch, decreased the amount of amylopectin, and formed more amylose with more free hydroxyl groups. The bond strength reached its maximum value when the amount of HCl was 23%.

CONCLUSIONS

1. Acid-hydrolysis destroyed the hydrogen bonds between starch molecules. The number of free hydroxyl groups first increased, and then decreased when the amount of acid was increased. The bond strength also increased at first, and then decreased with increased acid content, and the bond strength reached its maximum value when the amount of acid was 23%.
2. Acid-hydrolysis changed the crystalline structure of starch. The crystallinity of starch decreased when the amount of acid was increased. The crystallinity reached the minimum value when the amount of acid was 23%.
3. The surface of starch was corroded under acid-hydrolysis. The degree of corrosion was the lowest at 13% acid, but the corrosion was not significantly different when the amount of acid was increased from 18% to 33%. The compatibility between starch particles and PVA was the highest with 18% acid.
4. The heat resistance of starch-based adhesive first decreased, then increased with increased acid content.

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